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(54) **Stabilized polymeric organosilane compositions.**

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## Stabilized polymeric organosilane compositions

The present invention relates to stabilized polymeric organosilane compositions.

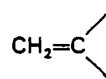
A relatively recent development in the field of coatings and adhesives has been the development of a class of materials which we shall refer to as polymeric organosilanes. These materials comprise organic polymer backbones having hydrolytically-reactive silyl groups pendent from the backbones. These types of compounds can be conveniently produced by interpolymerizing ethylenically unsaturated organic monomers, e.g. ethyl acrylate, vinyl acetate and the like, with ethylenically-unsaturated organosilane monomers having hydrolytically-reactive groups bonded to the silicon, e.g. vinyltrimethoxysilane and  $\gamma$ -methacryloxypropyltrimethoxysilane. Examples of such interpolymerized organosilanes are found in United States Patents Nos 3,408,420; 3,308,800; 3,542,585; 3,962,471; 3,062,242; and 3,577,399.

The polymeric organosilanes described above are useful as coating materials, or, in some instances, serve a function similar to that of a conventional coupling agent. In the latter case, the polymeric organosilanes are used in conjunction with conventional resinous coatings or adhesives to improve the compatibility and/or bonding between the resinous materials and inorganic oxide substrates or fillers. When the resinous material is a thermoplastic polymer containing essentially no chemically-reactive functionality, the polymeric organosilanes may provide adhesion promoting benefits which are superior to those provided by conventional monomeric organosilane coupling agents. This is due to the fact that conventional organosilanes rely on the reactivity of their organo moiety with complementarily reactive groups in the resin matrix to provide bonding, whereas the polymeric organosilanes are believed to provide bonding to the resin matrix by non-reactive mechanisms such as through-molecular entanglement with the molecules of the resin matrix and, to some extent, through Van Der Waals forces. Thus they do not require that the resin matrix contain reactive functional groups.

One of the major problems associated with the use of the polymeric organosilanes which has hindered their more widespread commercial use is their lack of shelf stability and potlife; that is, their tendency to undergo unacceptable viscosity increase or gelation prior to use. This lack of shelf stability is due to crosslinking reactions which take place at the pendent silyl groups of the polymeric organosilane molecules.

United States Patent No. 4,043,953 discloses a means of improving the stability, i.e. potlife, of a coating composition based on polymeric organosilanes which are produced by copolymerizing an acrylatosilane, methacrylato-

silane or vinyl silane with one or more vinyl-containing monomers, i.e. monomers containing the group



The coating compositions are stabilized against premature gelation by the addition thereto of from 0.5 to 15 percent based on the weight of the polymeric organosilane of a monomeric hydrolytically reactive silane of the formula  $\text{X}_n\text{Si}(\text{OR})_{(4-n)}$  wherein X is an organic radical having from 1 to 12 carbon atoms, R can be methyl, ethyl, 2-methoxymethyl, 2-ethoxyethyl, or an acyl group containing 5 or less carbon atoms, and n is 0, 1, or 2. It is believed that the addition of the monomeric silane stabilizes the polymeric silane coating composition by reacting with trace amounts of moisture and thereby preventing the moisture from hydrolyzing and crosslinking the polymeric organosilane.

While the method disclosed in United States Patent No. 4,043,953 undoubtedly improves the stability of polymeric organosilanes, we have found that this method has certain limitations, especially when one desires to employ the polymeric organosilanes as adhesion promoter additives, rather than as coatings *per se*. For a number of reasons for viscosity stability requirements are some-what more stringent when the polymeric organosilane is used as an adhesion promoter additive, rather than as a coating material. For example, when a copolymer of methyl methacrylate and gamma-methacryloxypropyltrimethoxysilane is employed as a coating composition, the gamma-methacryloxypropyltrimethoxysilane typically comprises about 5 to 10 weight percent of the copolymer. By contrast, when a copolymer of the same two monomers is to be employed as an adhesion promoter additive, the gamma-methacryloxypropyltrimethoxysilane typically comprises about 10 to 50 weight percent of the copolymer. Since only about one crosslink per 5,000 to 10,000 molecular weight units can cause the polymeric organosilane to gel, the relatively high silicon level which is desirable in polymeric organosilanes used as adhesion promoters increases the possibility of gelation by providing a relatively high number of sites for crosslinking.

When using a polymeric organosilane as a coating material, as disclosed in the aforementioned United States patent, No. 4,043,953, some viscosity increase is tolerable provided that the composition is fluid enough to be applied to a substrate. By contrast, even relatively minor viscosity increases can inhibit the effectiveness of the polymeric organosilane

when, for example, it is added to a thermoplastic adhesive to improve adhesion to an inorganic oxide substrate. To be effective, the adhesion promoter must migrate through the resin matrix to the substrate/adhesive interface and this becomes increasingly difficult as the viscosity of the adhesion promoter is elevated.

We have found that the addition of monomeric hydrolytically reactive silanes as stabilizers is not a very effective means of stabilizing the viscosity of a polymeric organosilane when the polymeric organosilane is exposed to moisture levels of the order of several thousand parts per million. Merely increasing the amount of monomeric hydrolytically reactive organosilane proportionately to the amount of water does not provide highly effective stabilization at these levels of water. Moreover, we have found that the amounts of monomeric hydrolytically reactive organosilane which would be required, on a stoichiometric basis, to scavenge water at levels of several thousand parts per million may impair the effectiveness of the polymeric organosilane as an adhesion promoter.

Since adhesion promoters are generally employed in small quantities, that is, of the order of a few weight percent of the resin to which they are added, they tend to be used rather slowly and may have to be stable over storage periods of several months. Moreover, they may be stored in containers which are frequently opened to remove small quantities and thus are highly susceptible to exposure to ambient moisture levels of the order of thousand of parts per million.

It is therefore, an object of this invention to provide a method of stabilizing a polymeric organosilane against viscosity increase or gelation in the presence of water without employing excessive amounts of monomeric hydrolytically reactive silanes that would impair the effectiveness of the polymeric organosilane as an adhesion promoter.

It is a further object of this invention to provide a highly stable polymeric organosilane composition, i.e. one which will not undergo gelation upon extended exposure to moisture levels of the order of several thousand parts per million.

There is provided in accordance with the teaching of this invention a highly stable polymeric organosilane composition comprising:

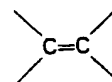
- (a) a polymeric organosilane;
- (b) a monomeric hydrolytically-reactive compound consisting of either (i) a monomeric hydrolytically-reactive organosilanes or (ii) a trialkyl orthoformate;
- (c) an alkanol having 1 to 4 carbon atoms.

Both the monomeric hydrolytically-reactive compound and the alkanol, individually, had a viscosity-stabilizing effect when added to polymeric organosilanes which were subsequently exposed to 2,000 p.p.m. of water. However, it

was totally unexpected that when both the monomeric hydrolytically-reactive compound and alkanol were admixed with the polymeric organosilane a synergistic effect was achieved whereby the stability of the polymeric organosilane, measured as the time to gelation in the presence of 2,000 p.p.m. of water, far exceeded that obtained by the use of either the monomeric hydrolytically-reactive compound or the alkanol as the sole stabilizer at similar concentrations.

The polymeric organosilane employed in the compositions of this invention is a copolymer of:

- (1) at least one ethylenically-unsaturated monomer containing at least one group of the formula



and

- (2) at least one ethylenically-unsaturated organosilane monomer of the formula  $\text{RSiX}_n\text{R}'_{(3-n)}$  wherein R is a monovalent organic radical containing a vinyl group, R' is a monovalent hydrocarbon radical containing up to 10 carbon atoms and is preferably alkyl, and n is an integer from 1 to 3, preferably 3; and X is a hydrolyzable group chosen from alkoxy of 1 to 4 carbon atoms, alkoxyalkoxy containing up to 6 carbon atoms, acyloxy of 2 to 4 carbon atoms, phenoxy, and oxime. Examples of ethylenically-unsaturated organosilane monomers are gamma-methacryloxypropyltrimethoxysilane, vinyl triethoxysilane, and vinyl-tris(2-methoxyethoxy) silane.

As merely illustrative of suitable ethylenically-unsaturated organic monomers useful in producing the polymeric organosilane one can mention alkyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, butyl methacrylate, 2-ethylhexyl methacrylate and lauryl methacrylate; vinyl aromatic hydrocarbons such as styrene, vinyl toluene and alpha-methyl styrene; vinyl halides and vinylidene halides such as vinyl chloride and vinylidene chloride; conjugated dienes such as butadiene and isoprene; and vinyl esters of saturated fatty acids having 1 to 12 carbon atoms such as vinyl acetate and vinyl propionate.

The ratio of ethylenically-unsaturated organic monomer to ethylenically-unsaturated organosilane lies within the limits of from 0.5 to 25 mole percent of the ethylenically-unsaturated organosilane and from 99.5 to 75 mole percent of the ethylenically-unsaturated organic monomer. When the polymeric organosilane is to be employed as an adhesion promoter additive; it is preferred that the polymeric adhesion promoter have polymerized therein from 5 to 20 mole percent of the ethylenically-unsaturated organosilane monomer and from

95 to 80 mole percent of the ethylenically-unsaturated organic monomer.

The monomeric hydrolytically-reactive organosilanes which are useful as the monomeric hydrolytically-reactive compound of this invention have the formula  $R''_{(4-x)}SiX_x$  wherein X is a hydrolyzable group,  $R''$  is a monovalent organic radical of from 1 to 12 carbon atoms, which may or may not contain a functional organic group, and x is an integer having a value from 1 to 4, and is preferably 3 or 4. The hydrolyzable group represented by X can be any of those previously mentioned as hydrolyzable groups in the ethylenically-unsaturated monomeric organosilane. Examples of suitable monomeric hydrolytically-reactive silanes are the following:

Ethyltriethoxysilane  
Aryltriethoxysilane  
Vinyltriethoxysilane  
Phenyltriethoxysilane  
Methyltriacetoxysilane  
Dimethyldiethoxysilane  
Methyltrimethoxysilane  
Methyltriethoxysilane  
Vinyl-tris (2-methoxyethoxy) silane  
Gamma-methacryloxypropyltrimethoxysilane  
Beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane  
Gamma-mercaptopropyltrimethoxysilane  
Gamma-glycidoxypropyltrimethoxysilane

The trialkyl orthoformates which are useful as the monomeric hydrolytically-reactive compound used in this invention have the formula  $HC(OR'')_3$  wherein  $R''$  in each occurrence is an alkyl group of 1 to 3 carbon atoms.

In the improved compositions of this invention, the monomeric hydrolytically-reactive compound is present at a concentration of from 0.5 to 25 parts by weight, preferably 5 to 20 parts by weight per 100 parts by weight of polymeric organosilane. The alkanol is present at a concentration of 2 to 50 parts by weight, preferably 10 to 30 parts by weight, per 100 parts by weight of polymeric organosilane.

The polymeric organosilane compositions of this invention are usually, though not necessarily, provided in the form of a solution of the composition in an organic solvent. Any known chemically-inert organic solvent can be employed such as, for example, toluene, methyl ethyl ketone, acetone or tetrahydrofuran. As used here, the term "chemically-inert organic solvent" excludes alcohols. The amount of solvent is not critical in any way.

Since the polymeric organosilane itself is frequently produced by solution polymerization techniques, the stabilized composition of this invention can be conveniently produced by admixing with the polymerization reaction product in the solvent medium the monomeric hydrolytically-reactive compound and alkanol in the aforementioned amounts.

The stabilized polymeric organosilane com-

positions of this invention can be employed as coating materials or they can be employed as adhesion promoter additives for resinous coatings or adhesives. When the compositions are employed as coating materials there can also be present in the compositions, in the usual known effective concentrations, such conventional additives as levelling agents, flattening agents, fillers, pigments, antioxidants, cure accelerating catalysts or flow control agents.

The improved compositions of this invention may also be employed as adhesion promoter compositions to improve the adhesion of thermoplastic resinous materials to inorganic oxide surfaces. As used herein, the term "inorganic oxide surfaces" includes aluminum and steel because their surfaces are oxidized even though their subsurfaces are not. Generally, the inorganic oxide materials which can be beneficially employed in conjunction with the improved compositions of this invention are any inorganic solid materials possessing either oxygen (chemisorbed or covalently bonded) or hydroxyl (bonded or free) at its exposed surface. The inorganic oxide material can be in any form, including particles of irregular or regular (e.g., spherical) shape, individual fibers, woven fiber mats or fabrics, of continuous surfaces such as sheets, slabs and formed shapes. Specific illustrations of suitably employed inorganic oxide surfaces are, for example, brass (with an oxidized surface), copper metal (oxidized at its surface), iron or steel (oxidized at its surface), alumina, aluminum trihydrate, siliceous materials such as fumed silica, hydrated silica (precipitated silica), silica aerogels, silica xerogels, aluminum silicates, calcium magnesium silicate, asbestos, glass fibers, clays, molecular sieves, Wollastonite, calcium carbonate, carbon black (including lamp black), titanium dioxide, calcium sulphate and magnesium sulfate.

The resinous medium with which the adhesion promoter can be suitably employed includes essentially any plastics or resin, including rubber compounds, for example suitable thermoplastic polyesters (e.g. polyethylene terephthalate, polybutylene terephthalate), polycarbonates, polyethylenes, polybutylenes, polystyrenes, styrene-butadiene copolymers, polypropylenes, ethylene propylene co- and terpolymers, silicone resins and rubbers, SBR rubbers, nitrile rubbers, natural rubbers, homopolymers and copolymers of acrylates and methacrylates (e.g. methyl methacrylate, ethyl acrylate or 2-ethylhexyl acrylate), polyvinyl halides such as polyvinyl chloride, homopolymers and copolymers of vinyl esters of fatty acids (e.g. polyvinyl acetate or polyvinyl butyrate), thermoplastic polyurethanes, polysulfones, polysulfide rubbers, nitrocelluloses, cellulose acetate, cellulose acetate butyrate, viscose rayon nylons or ethylene copolymers,

(e.g. ethylene-vinyl acetate, ethylene acrylic acid or ethylene-acrylate).

The adhesion promoter can be supplied directly to the surface of the inorganic oxide material prior to contacting the inorganic oxide material with the resinous medium or the adhesion promoter can be blended into the resinous medium and the resinous medium thereafter brought into contact with the inorganic oxide surface.

### Claims

1. A stabilized polymeric organosilane composition comprising:

(A) a polymeric organosilane compound having copolymerized therein:

(1) from 99.5 to 75 mole percent of an ethylenically unsaturated organic monomer and

(2) from 0.5 to 25 mole percent of an ethylenically-unsaturated organosilane monomer of the formula  $RSiX_nR'_{(3-n)}$  wherein R is a monovalent organic radical containing a vinyl group, R' is a monovalent hydrocarbon radical containing up to 10 carbon atoms, n is an integer from 1 to 3, and X is a hydrolyzable group chosen from alkoxy containing from 1 to 4 carbon atoms, alkoxyalkoxy containing up to 6 carbon atoms, acyloxy containing from 2 to 4 carbon atoms, phenoxy, and oxime;

(B) from 0.5 to 25 parts by weight, per 100 parts by weight of the polymeric organosilane compound, of either (a) a monomeric hydrolytically-reactive organosilane of the formula  $R''_{(4-x)}SiX_x$  wherein X is a hydrolyzable group as previously defined, R'' is a monovalent organic radical containing from 1 to 12 carbon atoms, and x is an integer from 1 to 4 or b) a trialkyl orthoformate of the formula  $HC(OR'')_3$  wherein R'' in each occurrence is an alkyl group of 1 to 3 carbon atoms; and

(C) from 2 to 50 parts by weight, per 100 parts by weight of the polymeric organosilane, of an alkanol having from 1 to 4 carbon atoms.

2. A composition as claimed in claim 1 wherein component (B) is present at a concentration of from 5 to 20 parts by weight and component (C) is present at a concentration of 10 to 30 parts by weight, per 100 parts by weight of the polymeric organosilane.

3. A composition as claimed in claim 1 or claim 2 wherein the polymeric organosilane is a copolymer of methyl methacrylate and gamma-methacryloxypropyltrimethoxysilane.

4. A composition as claimed in any one of the preceding claims wherein the composition is in the form of a solution in chemically-inert organic solvent.

### Revendications

1. Composition stabilisée d'organopolysiloxane, comprenant:

(A) un organopolysiloxane dans lequel sont incorporés par copolymérisation:

(1) 99.5 à 75 moles pour cent d'un monomère organique à non saturation éthylénique et

(2) 0.5 à 25 moles pour cent d'un organosilane monomère à non saturation éthylénique de formule  $RSiX_nR'_{(3-n)}$  dans laquelle R est un radical organique monovalent contenant un groupe vinyle, R' est un radical hydrocarboné monovalent contenant jusqu'à 10 atomes de carbone, n est un nombre entier de 1 à 3, et X est un groupe hydrolysable choisi entre des groupes alkoxy contenant 1 à 4 atomes de carbone, des groupes alkoxyalkoxy contenant jusqu'à 6 atomes de carbone, des groupes acyloxy contenant de 2 à 4 atomes de carbone, le groupe phénoxy et un groupe oxime;

(B) 0.5 à 25 parties en poids, pour 100 parties en poids de l'organopolysiloxane, (a) d'un organosilane monomérique à réaction hydrolytique de formule  $R''_{(4-x)}SiX_x$  dans laquelle X est un groupe hydrolysable tel que défini ci-dessus, R'' est un radical organique monovalent contenant 1 à 12 atomes de carbone et x est un nombre entier de 1 à 4; ou (b) un orthoformiate de trialkyle de formule  $HC(OR'')_3$  dans laquelle R'' est dans chaque cas un groupe alkyle ayant 1 à 3 atomes de carbone;

(C) 2 à 50 parties en poids, pour 100 parties en poids de l'organopolysiloxane, d'un alcanol ayant de 1 à 4 atomes de carbone.

2. Composition suivant la revendication 1, dans laquelle le composant (B) est présent à une concentration de 5 à 20 parties en poids et le composant (C) est présent à une concentration de 10 à 30 parties en poids, pour 100 parties en poids de l'organopolysiloxane.

3. Composition suivant la revendication 1 ou suivant la revendication 2, dans laquelle l'organopolysiloxane est un copolymère de méthacrylate de méthyle et de gamma-méthacryloxypropyltriméthoxysilane.

4. Composition suivant l'une quelconque des revendications précédentes, qui est sous la forme d'une solution dans un solvant organique chimiquement inerte.

### Patentansprüche

1. Stabilisiertes polymeres Organosilan enthaltende Masse aus

(A) einem polymeren Organosilan, hergestellt durch Copolymerisieren von

(1) 99,5 bis 75 mol.-% eines ethylenisch ungesättigten Monomeren und

(2) 0,5 bis 25 mol.-% eines ethylenisch ungesättigten Organosilans der allgemeinen Formel  $RSiX_nR'_{(3-n)}$ , worin R eine einwertige Vinylgruppe enthaltende organische Gruppe, R' eine einwertige Kohlenwasserstoffgruppe mit bis zu 10 C-

Atomen,  $n$  eine ganze Zahl von 1 bis 3 und  $X$  eine hydrolysierbare Gruppe in Form einer Alkoxygruppe enthaltend 1 bis 4 C-Atome, einer Alkoxyalkoxygruppe enthaltend bis zu 6 C-Atome, einer Acyloxygruppe enthaltend 2 bis 4 C-Atome, einer Phenoxy- oder Oximgruppe ist;

(B) 0,5 bis 25 Gew.-Teile—bezogen auf 100 Gew.-Teile polymeres Organosilan—von

- (a) einem monomeren hydrolytisch reaktiven Organosilan der allgemeinen Formel  $R''_{(4-x)}SiX_x$ , worin  $X$  obige hydrolysierbare Gruppe,  $R''$  eine einwertige organische Gruppe enthaltend 1 bis 12 C-Atome und  $x$  eine ganze Zahl von 1 bis 4 ist, oder
- (b) einem Trialkylorthoformiat der allgemeinen Formel  $HC(OR'')_3$ , worin  $R''$  jeweils eine Alkylgruppe mit 1 bis 3 C-Atomen ist, und

(C) 2 bis 50 Gew.-Teile—auf 100 Gew.-Teile polymeres Organosilan—eines Alkohols mit 1 bis 4 C-Atomen.

2. Masse nach Anspruch 1, dadurch gekennzeichnet, daß die Komponente (B) in einer Konzentration von 5 bis 20 Gew.-Teilen und die Komponente (C) in einer Konzentration von 10 bis 30 Gew.-Teilen auf 100 Gew.-Teile polymeres Organosilan enthalten sind.

3. Masse nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das polymere Organosilan ein Copolymer von Methylmethacrylat und  $\gamma$ -Methacryloxypropyltrimethoxysilan ist.

4. Masse nach Anspruch 1 bis 3, dadurch gekennzeichnet, daß die Masse in Form einer Lösung in einem chemisch inerten organischen Lösungsmittel vorliegt.

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